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(71)Applicant: NITTO KASEI CO LTD

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(72)Inventor: OKADA TAKAYUKI

**NAKAMURA HIROMASA** 

TABUCHI HITOSHI

MORI KIYOMI

#### (54) MOISTURE-CURABLE COMPOSITION AND POLY (DIALKYLSTANOXANE) DISILICATE **COMPOUND**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide moisture-curable compositions which quickly cure and, excel in adhesion and water-resistant adhesion.

SOLUTION: The moisture-curable compositions comprise, as the major components, (A) 100 pts.wt. silyl group-containing organic polymer having at least one silicon atom bonded to a hydrolyzable group at the molecular terminal or in the side chain in the molecule and (B) 0.1-10 pts.wt. curing catalyst which is composed of a reaction product of a poly(dialkylstanoxane) dicarboxylate represented by formula (1) with a silicate compound represented by the formula: R3nSi(OR4)4-n.



1/2 ページ

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## CLAIMS

[Claim(s)]

[Claim 1]a molecular terminal — or — a side chain — hydrolytic — a basis — having joined together — a silicon atom — one — a molecule — inside — at least — one — a piece — having — a silyl group — content — organicity — a polymer — (— A —) — 100 — a weight section — a curing catalyst — (— B —) — 0.1 – ten — a weight section — a basic component — carrying out — a constituent — setting — a curing catalyst (B) — following formula (1): [Formula 1]

(R<sup>1</sup> and R<sup>2</sup> among a formula) Even if it is a hydrocarbon group with 1-12 carbon atoms independently and two R<sup>1</sup> and R<sup>2</sup> of an individual (2m+2) are the same respectively, it may differ — m — one or more integers — it is — the poly (dialkyl stanoxane) dicarboxylate expressed and following formula (2):R<sup>3</sup> Si (OR<sup>4</sup>) <sub>4-n</sub> (2)

(R³ and R⁴ among a formula) Even if it is a hydrocarbon group with 1-4 carbon atoms independently and n R³ and R⁴ of an individual (4-n) are the same respectively, it may differ — n — an integer of 0-3 — it is — a moisture curing nature constituent consisting of a silicate compound expressed and/or a resultant with the hydrolyzate.

[Claim 2]A silicate compound by which a curing catalyst (B) is expressed with poly (dialkyl stanoxane) dicarboxylate expressed with a general formula (1), and a general formula (2), and/or a resultant with the hydrolyzate, The moisture curing nature constituent according to claim 1 being a silicate compound expressed with a general formula (2), and/or a mixture with the hydrolyzate.

[Claim 3]A curing catalyst (B) is a following formula (3). : [Formula 2]  $$\rm R^2$ 

3

The poly (dialkyl stanoxane) JISHIRIKETO compound expressed with (the inside of a formula,  $R^2$ ,  $R^4$ , and m are the same as the above), Or the moisture curing nature constituent according to cleim 1 being a mixture with this poly (dialkyl stanoxane) JISHIRIKETO compound, tetra alkoxysilane, and/or its

[Claim 4]A following formula (3) : [Formula 3]

nydrolyzate

JP,2001-139820,A [CLAIMS]

2/2ページ

(Among a formula, R<sup>2</sup> is a hydrocarbon group with 1-12 carbon atoms, may be the same respectively, or may differ, and R<sup>4</sup>) [ of R<sup>2</sup> of an individual (2m+2) ] it is a hydrocarbon group with 1-4 carbon atoms, and six R<sup>4</sup> may be the same or may differ — m — one or more integers — it is — the poly (dialkyl stanoxane) JISHIRIKETO compound expressed.

[Translation done.]

JP,2001-139820,A [DETAILED DESCRIPTION]

2/10 ページ

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# DETAILED DESCRIPTION

[Detailed Description of the Invention]

Field of the Invention]This invention relates to the moisture curing nature constituent and poly (dialkyl stanoxane) JISHIRIKETO compound which hardened promptly and were excellent in an adhesive property and waterproofing adhesive property.

quick hardening, and it is excellent that there are no necessities, such as mixed adjustment of liquid, etc. Description of the Prior ArtJAs 1 liquid type moisture curing nature rubber, silicone rubber, urethane ubber, polysulfide rubber, etc. are known. Generally 1 liquid type moisture curing nature rubber has in respect of workability compared with the two-component thing.

adhesive property, especially waterproofing adhesive property are remarkably inferior, and need to use a primer etc. By JP,59–38989,B, JP,1–58219,B, JP,2–22105,B, JP,58–57460,A, JP,63–18975,B, etc. As a hardenability, there is little stain resistance to the circumference, and there is no toxicity. There is little stain resistance to the circumference compared with the usual silicone series rubber, and the paintwork known as a curing catalyst of the polymer which has this hydrolytic silicon group, in these catalysts, an Problem(s) to be Solved by the Invention]However, the thing of silicone series rubber has a problem in curing catalyst of the polymer which it has, a hydrolytic silicon group use of the resultant of dialkyl tin tooling product which hardens quickly and changes to a rubber-like substance (JP,62-35421,B, JP,61respect of the possibility of the contamination to the circumference, and the paintwork to the surface, state of a curing catalyst for a long period of time, When it exposes to humidity, it is 1 liquid setup-of-141761,A, JP,1-58219,A). This polymer has storage stability, weatherability, fizz-proof, and good color main chain, and for which a bridge can be constructed and it is stability under seal in the coexistence system rubber is a polymer which has a hydrolytic silicon functional group which uses polyether as a and the thing of urethane system rubber has a problem in respect of storage stability, weatherability, fizz-proof, discoloration, etc. There is a problem in respect of hardenability and the possibility of the contamination to the circumference also about polysulfide system rubber. Although modified silicone to the surface is good. Although a titanate compound, a tin carboxylate compound, amine, etc. are oxide or carboxylate, and alkoxysilane, in JP,7-11155,A, using a dibutyl tin screw (TORIETOKISHI fastness compared with a polyurethane system, compared with a polysulfide system, it excels in silicate) as a curing catalyst is proposed. Although the cure rate became quick by use of these development of the catalyst with a cure rate that it is not enough and still quicker was desired. ORGANO tin silicate compounds compared with the time of using ORGANO tin carboxylate,

(-- A --) -- 100 -- a weight section -- a ouring catalyst -- (-- B --) -- 0.1 - ten -- a weight section inside — at least — one — a piece — having — a silyl group — content — organicity — a polymer — Means for Solving the Problem] Then, this invention persons inquire wholeheartedly so that they may get a moisture curing nature constituent which hardened promptly and was excellent in an adhesive -- a basio component -- carrying out -- a constituent -- setting -- a curing catalyst -- (-- B --). (0005]namely, -- a claim -- one -- starting -- an invention -- a molecular terminal -- or -- a side ohain -- hydrolytio -- a basis -- having joined together -- a silicon atom -- one -- a molecule --property and waterproofing adhesive property, and they came to complete this invention. Following formula (1) : [0006] http://www4.ipdl.inpit.go.jp/cgi-bin/tran\_wab\_cgi\_ejje?atw\_u=http%3A%2F%2Fwww4.ipdl.inpi... 2008/06/27

 $\exists$ R<sup>1</sup>CO-S<sub>n</sub>-O-(S<sub>n</sub>-O-)<sub>m</sub>CR<sup>1</sup> | | | | |

independently and two R<sup>1</sup> and R<sup>2</sup> of an individual (2m+2) are the same respectively, it may differ -- m -- one or more integers -- it is -- the poly (dialkyl stanoxane) dicarboxylate expressed and following [0007](R<sup>1</sup> and R<sup>2</sup> among a formula) Even if it is a hydrocarbon group with 1-12 carbon atoms formula (2):R3 Si(OR4) 4-n (2)

( ${
m R}^3$  and  ${
m R}^4$  among a formula) Even if it is a hydrocarbon group with 1–4 carbon atoms independently and n  $\rm R^3$  and  $\rm R^4$  of an individual (4-n) are the same respectively, it may differ — n — an integer of 0-3 — it is -- it is related with a moisture curing nature constituent consisting of a silicate compound expressed and/or a resultant with the hydrolyzate.

constituent according to claim 1 being a silicate compound expressed with a general formula (2), and/or general formula (2) and/or a resultant with the hydrolyzate, It is related with the moisture curing nature stanoxane) dicarboxylate to which a curing catalyst (B) is expressed with a general formula (1), and a [0008]A silicate compound by which an invention concerning claim 2 is expressed with poly (dialkyl a mixture with the hydrolyzate.

[0009]in an invention which furthermore relates to claim 3, a curing catalyst (B) is a following formula

[Formula 5]

(3)  $(R^4O)_3S1O-Sn-O-(Sn-O-)_mSi_(OR^4)_3$  [0011]The poly (dialkyl stanoxane) JISHIRIKETO compound expressed with (the inside of a formula, R<sup>2</sup>, according to claim 1 being a mixture with this poly (dialkyl stanoxane) JISHIRIKETO compound, tetra R<sup>4</sup>, and m are the same as the above), Or it is related with the moisture curing nature constituent alkoxysilane, and/or its hydrolyzate.

[0012]An invention which furthermore relates to claim 4 is a following formula (3). : [0013] [Formula 6]

(3)  $(R^4O)_3S1O-Sn-O-(Sn-O-)_mS1 (OR^4)_3$ 

respectively, or may differ, and  $R^4$ ) [ of  $R^2$  of an individual (2m+2) ] it is a hydrocarbon group with 1-4 carbon atoms, and six  $R^4$  may be the same or may differ -- m -- one or more integers -- it is -- it is [0014](Among a formula,  $\mathbb{R}^2$  is a hydrocarbon group with 1–12 carbon atoms, may be the same related with the poly (dialkyl stanoxane) JISHIRIKETO compound expressed.

chain the organic polymer (A) used for this invention with the hydrolytic basis. It is a silyl group content hydrolytic basis) and ] in [ at least one ] one molecule, and an alkylene oxide polymer thru/or polyether, [Embodiment of the Invention] The silicon atom which combined with the molecular terminal or the side an ether ester block copolymer, etc. are mentioned as a main chain of this polymer. The polymer of an organicity polymer which it has [ (it may be hereafter called the silicon group combined with the

(0.016] As said alkylene oxide polymer thru/or polyether,  $(\mathrm{CH_2CH_2O})$  What has repeating units, such as p (0017]As a polymer of an ethylene nature unsaturated compound and diene series, Homopolymers, such (CHCH<sub>3</sub>CH<sub>2</sub>O) p(CHC<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>O) p(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O) p. is illustrated. Here, p is two or more integers. mentioned. More specifically Polybutadiene, a styrene butadiene copolymer, An acrylonitrile butadiene isobutylene-isoprene copolymer, Polychloroprene, a styrene chloroprene copolymer, an acrylonitrile copolymer, an ethylene-butadiene copolymer, Ethylene propylene rubber, an ethylene-vinylacetate isobutylene, butadiene, isoprene, and chloroprene, or two or more sorts of these copolymers are copolymer, an ethylene-acrylic ester copolymer, Polyisoprene, a styrene isoprene copolymer, an as ethylene, propylene, acrylic ester, methacrylic acid ester, vinyl acetate, acrylonitrile, styrene, chloroprene copolymer, polyisobutylene, polyacrylic ester, polymethacrylic acid ester, etc. are athylene nature unsaturated compound and diene series is mentioned.

molecule, or may exist in the side chain. Even if the silicon group combined with the hydrolytic basis has hardened material nature, and there are 1.5 or more pieces with one piece although it is good. A method Furthermore, the hydrolytic basis and the non-hydrolytic basis may combine with one silicon atom. As a group combined with the hydrolytic basis is chosen from the range of 1-3. The number of the hydrolytic groups (mono- alkoxy silyl groups, a dialkoxy silyl group, and the Tori alkoxy silyl groups.are included) is few polymers per molecule, it is preferred that it averages per molecule from a point of a cure rate and publicly known as a method of combining with said main chain polymer the silicon group combined with group, an amino silyl group, an amino oxysilyl group, an oxime silyl group, and an amide silyl group are silicon group combined with the hydrolytic basis, handling is an easy point, and especially alkoxy silyl mentioned. Here, the number of these hydrolytic bases combined with the silicon atom in the silicon 0018]The silicon group combined with the hydrolytic basis is a basis which causes a condensation Specifically, a halogenation silyl group, alkoxy silyl groups, an alkenyl oxysilyl group, an acyloxy silyl preferred. The silicon group combined with the hydrolytic basis may exist in the end of a polymer eaction by using a catalyst etc. if needed under existence of humidity and a cross linking agent. bases combined with one silicon atom may be one, and that of them may be [ two or more ]. the hydrolytic basis is employable.

manufactured by a publicly known method, commercial items, such as KANEKA MS polymer by Kaneka [0019]Aithough the molecular weight of the organic polymer (A) used by this invention does not have restrictions in particular, the thing of the amount of polymers is hyperviscosity, and since it becomes desirable [ a thing ] as a number average molecular weight. Although such an organic polymer can be difficult [ a use top ] when it is considered as a hardenability constituent, 30000 or less are too Corp., may be used for it, for example.

(0020]One sort of the silicate compound expressed with the dialkyl tin oxydi carboxylate expressed with a general formula (1) and a general formula (2) as a curing catalyst (B) used for this invention and/or a resultant with the hydrolyzate or two sorts or more are used preferably.

replacing, or a substituted phenyl group is mentioned. Two  $\mathbb{R}^1$  may be the same and may differ.  $\mathbb{R}^2$  of an individual may be the same and may differ (2m+2). Although m should just be one or more integers, it is [0021]In said general formula (1), as a hydrocarbon group with 1-12 carbon atoms expressed with  $\mathbb{R}^1$ and R<sup>2</sup>, Straight chain shape, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, decyl, and lauryl, or a branched chain-like alkyl group, unan integer of 1-3 preferably.

tetracotyl-1,3-bis(butyryloxy)distannoxane, 1,1,3,3-tetracctyl-1,3-bis(octancyloxy)distannoxane, 1,1,3,3distannoxane, 1,1,3,3-tetramethyl 1,3-bis(lauroyl oxy)distannoxane, 1,1,3,3-tetrabuthyl 1,3-bis(acetoxy) 1,1,3,3-tetramethyl 1,3-bis(octanoyloxy)distannoxane, 1,1,3,3-tetramethyl 1,3-bis(2-ethylhexanoyl oxy) 1,1,3,3-tetramethyl 1,3-bis(acetoxy)distannoxane, 1,1,3,3-tetramethyl 1,3-bis(butyryloxy)distannoxane, [0022]if the dialkyl tin oxydi carboxylate expressed with a general formula (1) is illustrated concretely. distannoxane, 1,1,3,3-tetra lauryl 1,3-bis(acetoxy)distannoxane, 1,1,3,3-tetra lauryl 1,3-bis(butyryloxy) tetrabuthyl 1,3-bis(lauroyl oxy)distannoxane, 1,1,3,3-tetraoctyl-1,3-bis(acetoxy)distannoxane, 1,1,3,3ethylhexanoyl oxy)distannoxane, Tetra alkyl distannoxane dicarboxylates, such as 1,1,3,3-tetra lauryl distannoxane, 1,1,3,3-tetra lauryl 1,3-bis(octanoyloxy)distannoxane, 1,1,3,3-tetra lauryl 1,3-bis(2-(ootanoyloxy)distannoxane, 1,1,3,3-tetrabuthyl 1,3-bis(2-ethylhexanoyl oxy)distannoxane, 1,1,3,3distannoxane, 1,1,3,3-tetrabuthyl 1,3-bis(butyryloxy)distannoxane, 1,1,3,3-tetrabuthyl 1,3-bis tetracotyl-1,3-bis(2-ethylhexancyl oxy)distannoxane, 1,1,3,3-tetracctyl-1,3-bis(laurcyl oxy)

JP,2001-139820,A [DETAILED DESCRIPTION]

1,5-bis(lauroyl oxy)tris TANOKISAN, 1,1,3,3,5,5-hexa lauryl 1,5-bis(acetoxy)tris TANOKISAN, 1,1,3,3,5,5hexamethyl 1,5-bis(lauroyl oxy)tris TANOKISAN, 1,1,3,3,5,5-hexabutyl-1,5-bis(acetoxy)tris TANOKISAN, distannoxane were preferred, and generated among these. They are 1,1,3,3-tetrabuthyl 1,3-bis(acetoxy) 1,1,3,3,5,5-hexabutyl-1,5-bis(butyryloxy)tris TANOKISAN, 1,1,3,3,5,5-hexabutyl-1,5-bis(octanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexaootyl-1,5-bis(2-ethylhexanoyl oxy)tris TANOKISAN, 1,1,3,3,5,5-hexaoctyl-TANOKISAN, 1,1,3,3,5,5-hexabutyl-1,5-bis(2-ethylhexanoyl oxy)tris TANOKISAN, 1,1,3,3,5,5-hexabutyl-, 5-bis(lauroyl oxy)tris TANOKISAN, 1,1,3,3,5,5-hexaoctyl-1,5-bis(acetoxy)tris TANOKISAN, 1,1,3,3,5,5mentioned. Four or less carboxylate with a number of carbon atoms is more preferred from the ease of TANOKISAN, 1,1,3,3,5,5-hexa lauryl 1,5-bis(2-ethylhexanoyl oxy)tris TANOKISAN, Hexa- RUKIRUTORI stanoxane dicarboxylates, such as 1,1,3,5,5-hexa lauryl 1,5-bis(lauroyl oxy)tris TANOKISAN, etc. are ,3-bis(lauroy) oxy)distannoxane, 1,1,3,5,5-hexamethyl 1,5-bis(acetoxy)tris TANOKISAN, 1,1,3,3,5,5removal of the carboxylate which tetrabuthyl diacyl oxydi stanoxane and tetra OKUCHIRUJI acyloxy нехатеthyl 1,5-bis(butyryloxy)tris TANOKISAN, 1,1,3,3,5,5-hехатеthyl 1,5-bis(octanoyloxy)tris FANOKISAN, 1,1,3,3,5,5-hexamethyl 1,5-bis(2-ethylhexanoyl oxy)tris TANOKISAN, 1,1,3,3,5,5hexa lauryl 1,5-bis(butyryloxy)tris TANOKISAN, 1,1,3,3,5,5-hexa lauryl 1,5-bis(octanoyloxy)tris hexaoctyl-1,5-bis(butyryloxy)tris TANOKISAN, 1,1,3,3,5,5-hexaoctyl-1,5-bis(octanoyloxy)tris distannoxane or 1,1,3,3-tetraoctyl-1,3-bis(acetoxy)distannoxane still more preferably.

(0024]As a silicate compound made to react to the poly (dialkyl stanoxane) dicarboxylate expressed with butyl, and t-butyl, etc. are mentioned as a hydrocarbon group with 1-4 carbon atoms expressed with  $\mathsf{R}^3$ TORIETOKISHI methylsilane, a TORIETOKISHI ethylsilane, a TORIETOKI Cipro pill silane, doria, such as a Tori ethoxy-SOPUROPIRU silane and a TORIETOKISHI butylsilane, — a RUKOKISHI monoalkyl silane TORIPURO pill silane, an ethoxy triisopropyl silane, and an ethoxy tributylsilane, or the hydrolyzate of and  $\mathsf{R}^4$  , n  $\mathsf{R}^3$  may be the same and may differ.  $\mathsf{R}^4$  of an individual may be the same or may differ (4-n). or its hydrolyzate. Diethoxy dimethylsilane, diethoxy diethylsilane, a diethoxydipropylsilane, A dialkoxy [0023]in a general formula (2), alkyl groups, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, shydrolyzate can be used. Specifically A tetramethoxy silane, a tetraethoxysilane, tetra propoxysilane, dialkyl silane or its hydrolyzates, such as a diethoxydiisopropylsilane and a diethoxydibutylsilane, said general formula (1), the silicate compound expressed with a general formula (2) and/or its Monoalkoxy trialkyl silanes, such as ethoxy trimethylsilane, an ethoxy triethylsilane, an ethoxy those is mentioned. Tetra alkoxysilane or its hydrolyzate is [ among these ] preferred. It is a Tetra alkoxysilane or its hydrolyzates, such as tetra isopropoxysilane and tetra butoxysilane, tetraethoxysilane still more preferably.

can be performed under existence of a solvent or absence, it is preferred to usually carry out under the preferred to make 1 Eq or more of alkoxy groups react, and to vanish a carboxyl group thoroughly to 1 Eq of carboxyl groups. If the carboxyl group remains, catalytic activity will fall. Although said reaction obtained by removing the carboxylate to generate under decompression. As for a reaction ratio, it is formula (2) and/or its hydrolyzate are made to react at 100-130 \*\* for about 1 to 3 hours, and it is dicarboxylate, a silicate compound, and/or a resultant with the hydrolyzate, The silicate compound shown by the poly (dialkyl stanoxane) dicarboxylate shown by a general formula (1) and a general [0025]The poly (dialkyl stanoxane) JISHIRIKETO compound which are poly (dialkyl stanoxane) absence of a solvent.

hydrolyzate, etc., although the resultant acquired differs in the structure of a resultant, Following general [0026]With a preparation rate with poly (dialkyl stanoxane) dicarboxylate, a silicate compound, and/or its shown by a general formula (2) to 1 mol of poly (dialkyl stanoxane) dicarboxylate a desirable resultant is formula (4) obtained by making 2-6 mol of 2 mol or more react preferably in the silicate compound ndicated to be by a general formula (1): [0027] [Formula 7]

(R4O) 3-n SiO-Sn-O- (Sn-O-) mSi (OR4) 3-n R<sub>2</sub>

3

[0028]It is a poly (dialkyl stanoxane) JISHIRIKETO compound expressed with (the inside of a formula,

 $R^2,\,R^3,\,R^4,\,m,$  and n are the same as the above).

[0029]As opposed to 1 mol of poly (dialkyl stanoxane) dicarboxylate a more desirable resultant is indicated to be by a general formula (1). Following general formula (3) obtained by making 2-6 mol react preferably 2 mol or more in a tetraalkyl silicate compound among the silicate compounds shown by a general formula (2): [0030]

[Formula 8]

[0031]It is a poly (dialkyl stanoxane) JISHIRIKETO compound expressed with (the inside of a formula,  $R^2$ ,  $R^4$ , and m are the same as the above). The poly (dialkyl stanoxane) JISHIRIKETO compound expressed with a general formula (3) is a new molecular entity.

[0032]Although a resultant of this invention has dramatically high catalytic activity compared with the conventional dialkyl tin compound, it is preferred to mix and use a silicate compound expressed with a general formula (2) and/or its hydrolyzate from the stability of a catalyst and an ease of handling, and the mixture ratio, When making both total quantity into 100 weight sections, it is desirable although it is a silicate compound and/or its one to hydrolyzate 99 weight section to 99 to resultant 1 weight section. They are a silicate compound and/or its ten to hydrolyzate 50 weight section to 90 to resultant 50 weight section to 90 to resultant 50 compound and/or its hydrolyzate, they are obtained, or they can be obtained also by the reaction of a silicate compound of an overlarge, and/or its hydrolyzate as dialkyl tin oxydi carboxylate. (B) has 0.1 – [0033]In a moisture curing nature constituent of this invention, content of a curing catalyst (B) has 0.1 –

Silicate compound of an overlate, and of the process of hardening performance is [ quantity of a curing catalyst (B) ] insufficient and it exceeds said range on the other hand, physical properties, such as recovery of a hardened material after hardening and weatherability, may worsen.

[0034]In order to promote hardening in a moisture curing nature constituent of this invention and to improve adhesion to a substrate, Can use publicly known various amino group substitution alkoxy silane compounds or a condensate of those, and specifically, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, N-(trimethoxysilylpropyl) ethylenediamine, delta-aminobutyl (methyl) diethoxysilane, N.N-bis(trimethoxysilylpropyl)ethylenediamine, these partial hydrolysates, etc. are

are mentioned. As other additive agents, adhesion grant agents, such as phenol resin and an epoxy resin, a silicic acid anhydride, hydrous silicic acids, clay, Calcination clay, glass, bentonite, organic bentonite, a dripping inhibitor, hydrogenation castor oil, a silicic acid anhydride, organic bentonite, colloidal silica, etc. agent, specifically For example, calcium carbonate, kaclin, talc, Fumed silica, sedimentation nature silica, zino oxide, magnesium oxide, a titanium dioxide, etc. are mentioned. Specifically as colorant, iron oxide, plasticizer, a hardening accelerator, a concrete retarder, a dripping inhibitor, an antiaging agent, and a milt balloon, glass fiber, asbestos, grinding quartz, diatomite, aluminum silicate, aluminium hydroxide, a carbon black, copper phthalocyanine blue, Phthalocyanine Green, etc. are mentioned. As a plasticizer, aliphatic-carboxylic-acid ester species, such as butyl oleate, and pentaerythritol ester. Epoxy system plasticizers, such as phosphoric ester, such as trioctyl phosphate and tricresyl phosphate, epoxidized soybean oil, and epoxy steario acid benzyl, a chlorinated paraffin, etc. are mentioned. Specifically as a (0035)Additive agents usually added by hardenability constituent, such as a bulking agent, colorant, a specifically Dibutyl phthalate, dioctyl phthalate, Phthalic ester, such as butylbenzyl phthalate, dioctyl an ultraviolet ray absorbent, radical chain inhibitor, a peroxide decomposition agent, various kinds of solvent, may be further added to a moisture curing nature constituent of this invention. As a bulking adipate, Succinio acid dioctyl, succinio acid diisodecyl, diisodecyl sebacate, Glycol ester, such as antiaging agents, etc. are mentioned.

[0036]

Example]Although an example is given to below and this invention is concretely explained to it, the range of this invention is not limited by this.

http://www4.ipdl.inpit.go.jp/cgi-bin/tran\_web\_cgi\_ejje?atw\_u=http%3A%2F%2Fwww4.ipdl.inpi... 2008/06/27

# JP,2001-139820,A [DETAILED DESCRIPTION]

[0037]Example of manufacture I thermometer, a reflux condenser, and an agitator in the 500-ml 4 Thu mouth flask which it had under a nitrogen air current, 49.8 g (0.2 mol) of dibutyltin oxide, the acetic anhydride 10.4g (0.1 mol), And after teaching 200 g of toluene and making it react at 112 \*\* for 2 hours, toluene was distilled off under decompression and 1.1.3.3-tetrabuthyl 1.3-bis(acetoxy)distannoxane was obtained (this compound was obtained quantitatively). Subsequently, taught 41.7 g (0.2 mol) of tetraethoxysilanes (ethyl ortho silicate), it was made to react at 120 \*\* for 3 hours, the ethyl acetate generated under decompression was distilled off, and tin compound A 79.8g (yield it is the same as that of the value based on 95% and tin oxide and the following) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [ -¹ and ] From the result of disappearance of 1559-cm<sup>-1</sup>, and absorption (477-cm<sup>-1</sup>) of Sn-O-Sn and the next ultimate analysis, it checked that they were the 1, 1, 3, and 3-tetrabuthyl 1 and 3-bis(TORIETOKISHI siloxy)distannoxane.

C(%) H(%) O(%) Si(%)Sn(%)

Measured value 40.1 7.7 17.0 6.9 28.3 theoretical values 40.0 7.9 17.1 6.7 28.3[0038]In the same 4 mouth flask as the example 1 of example of manufacture 2 manufacture, 74.7 g (0.3 mol) of dibutyltin oxide, The acatic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught, React and process like the example 1 of manufacture, and 1.1, 3, 3, 5, and 5-hexabutyl- 1 and 5-bis(acetoxy)tris TANOKISAN are obtained, Subsequently, 41.7 g (0.2 mol) of ethyl ortho silicate was prepared, it reacted and processed like the example 1 of manufacture, and the tin compound B102.4g (94% of yield) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [ -¹ and ] From the result of disappearance of 1559-cm<sup>-1</sup>, and absorption (477-cm<sup>-1</sup>) of Sn-O-Sn and the next ultimate analysis, it checked that they were 1, 1, 3, 5, and 5-hexabutyl- 1 and 5-bis(TORIETOKISHI siloxy)tris

C(%) H(%) O(%) Si(%)Su(%)

Measured value 39.9 7.7 14.6 5.1 32.9 theoretical values 39.7 7.8 14.7 5.1 32.7[0039]In the same 4 mouth flask as the example 1 of example of manufacture 3 manufacture, 72.2 g (0.2 mol) of dioctyl tin oxide, The acetic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught, it reacted and processed like the example 1 of manufacture, and 1. 1, 3, and 3-tetracotyl- 1 and 3-bis(acetoxy)distannoxane were obtained, subsequently prepared 41.7 g (0.2 mol) of ethyl ortho silicate, it was made to react at 120 \*\* for 3 hours, and tin compound C 101.2g (97% of yield) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [ -¹ and ] From the result of disappearance of 1559-cm<sup>-1</sup>, absorption (477-cm<sup>-1</sup>) of Sn-O-Sn, and the next ultimate analysis, it checked that they were 1, 1, 3, and 3-tetracotyl- 1 and 3-bis(TORIETOKISHI siloxy)distannoxane.

Measured value 49.6 9.4 13.6 5.2 2.2 theoretical values 49.6 9.3 13.5 5.3 22.3[0040]In the same 4 mouth flask as the example 1 of example of manufacture 4 manufacture, 108.3 g (0.3 mol) of dioctyl tin oxide.

The acetic anhydride 10.2g (0.1 mol) and 200 g of toluane are taught, React and process like the example 1 of manufacture, and 1. 1, 3. 3, 5, and 5-hexacotyl- 1 and 5-bis(acetoxy)tris TANOKISAN are obtained. Subsequently, 41.7 g (0.2 mol) of ethyl ortho silicate was prepared, it reacted and processed like the example 1 of manufacture, and tin compound D 135.5g (95% of yield) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [-1 and ] From the result of disappearance of 1559-cm<sup>-1</sup>, and absorption (477-cm<sup>-1</sup>) of Sn-O-Sn and the next ultimate analysis, it checked that they were 1, 1, 3, 3, 5, and 5-hexacotyl- 1 and 5-bis(TORIETOKISHI siloxy)tris

C(%) H(%) O(%) Si(%)Su(%)

Measured value 50.4 9.5 11.2 3.8 25.1 theoretical values 50.5 9.4 11.2 3.9 25.0[0041]In the same 4 mouth flask as the example 1 of example of manufacture 5 manufacture, 33.0 g (0.2 mol) of dimethyl tin oxide, The acetic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught, it reacted and processed like the example 1 of manufacture, and 1, 1, 3, and 3-tetramethyl 1 and 3-bis(acetoxy)distannoxane were obtained, subsequently 41.7 g (0.2 mol) of ethyl ortho silicate was prepared, it reacted and processed like the example 1 of manufacture, and tin compound E 63.8g (95% of yield) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [-¹ and ] From the result of disappearance of 1559-cm<sup>-1</sup>, and absorption (477-cm<sup>-1</sup>) of Sn-O-Sn and the next ultimate analysis, it checked that they were 1, 1, 3, and 3-tetramethyl 1 and 3-bis(TORIETOKISHI siloxy)distannoxane. C(%) H(%) O(%) Si(%)Sn(%)

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lask as the example 1 of example of manufacture 6 manufacture, 74.7 g (0.3 mol) of dibutyltin oxide, The 28.2 g of ethyl ortho silicate was added, the stirring dissolution was carried out, and the mixture F of the Measured value 28.6 6.2 21.6 8.5 35.1 theoretical values 28.6 6.3 21.4 8.4 35.3[0042]In the same 4 mouth obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [ -1 and ] From the result of ight yellow fluid which is a mixture of 80:20 (weight ratio) of 1, 1, 3, 3, 5, and 5-hexabutyl- 1, and 5-bis soetic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught, React and process like the example 1 of manufacture, and 1, 1, 3, 3, 5, and 5-hexabutyl- 1 and 5-bis(acetoxy)tris TANOKISAN are obtained, disappearance of 1559-cm<sup>-1</sup>, and absorption (477-cm<sup>-1</sup>) of Sn-O-Sn and the next ultimate analysis. FANOKISAN (it is the same as the object compound of the example 2 of manufacture), Furthermore Subsequently, 41.7 g (0.2 mol) of ethyl ortho silicate was prepared, it reacted and processed like the After checking that they are 1, 1, 3, 3, 5, and 5-hexabutyl- 1 and 5-bis(TORIETOKISHI siloxy)tris example 1 of manufacture, and the tin compound 104.6g (96% of yield) of the light yellow fluid was TORIETOKISHI siloxy)tris TANOKISAN and ethyl ortho silicate was obtained.

fANOKISAN are obtained, Subsequently, prepared 62.6 g (0.3 mol) of ethyl ortho silicate, it was made to obtained. This reaction mixture is absorption (1638 cm) of tin carbonyl at FT-IR. [ <sup>-1</sup> and ] The ullage of ,0043]in the same 4 mouth flask as the example 1 of example of manufacture 7 manufacture, 74.7 g (0.3 mol) of dibutyltin oxide, The acetic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught, React and of Sn-O-Sn and gas-chromatograph analysis, it checked that it was a mixture of 80.20 (weight ratio) of 1, 1, 3, 3, 5, and 5-hexabutyl- 1, and 5-bis(TORIETOKISHI siloxy)tris TANOKISAN (it is the same as process like the example 1 of manufacture, and 1, 1, 3, 5, and 5-hexabutyl- 1 and 5-bis(acetoxy)tris sthyl ortho silioate is quantified by disappearance of 1559-cm<sup>-1</sup>, and the check of absorption (477-cm<sup>-</sup> eact at 120 \*\* for 3 hours, and the reaction mixture G91.7g (95% of yield) of the light yellow fluid was the object compound of the example 2 of manufacture) and ethyl ortho silicate.

[0044]in the same 4 mouth flask as the example 1 of example of manufacture 8 manufacture, 49.8 g (0.2 nol) of dibutylkin oxide, The acetic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught, React and which are used as a hardening agent of C, D, E, F, G, H (F and G are mixtures with a silicate compound) 97.1g (95% of yield) of the light yellow fluid was obtained. This compound has checked disappearance of [0045]To Examples 1-8 and the comparative example 1 - 3 silyl-group content organicity polymer (MS oolymer S303 by Kaneka Corp.). The tin compounds A and B obtained in the examples 1, 2, 3, 4, 5, 6, 7, obtained, Subsequently, ethyl silicate 40 (poly silicic acid ethyl ester by Tama Chemicals Co., Ltd. (4 oatalytic activity examination and \*\*\*\* adhesive property examination were done. A result is shown in etraethoxysilicate, it reacted and processed like the example 1 of manufacture, and tin compound H sbsorption (1838-cm<sup>-1</sup>, 1559-cm<sup>-1</sup>) of tin carbonyl, and absorption (477-cm<sup>-1</sup>) of Sn-O-Sn in FT-IR. and 8 of manufacture. Three sorts of conventional tin compounds and other various additive agents or modified silicone were added in the blending ratio shown in Table 1, it kneaded at 25 \*\*, and the process like the example 1 of manufacture, and 1,1,3,3-tetrabuthyl 1,3-bis(acetoxy)distannoxane is pentamer)) 49.8g (from an ethoxy cardinal number) [ convert and ] It taught fairly about 0.2 mol of hardenability constituent was prepared. About the obtained hardenability constituent, a following able 2.

ectivity test aforementioned each hardenability constituent, and a snap time (time until it half-gels and CF. Material fracture TCF.material thin-layer fracture AF. Adherend-material interfacial peeling [0048] 0046]it was promptly neglected under the atmosphere of 25 \*\* and 60%RH after preparing catalytic preparing \*\*\*\* adhesive property test aforementioned each hardenability constituent. The aluminum 0047]The \*\*\*\* adhesive property examination based on JIS A 5758 was presented promptly after plate was used as adherend. The following cable addresses showed the fracture situation. mobility is lost), and tack free time (time until surface tackiness is lost) were measured. (Table 1)

JP,2001-139820,A [DETAILED DESCRIPTION]

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Table 2] [0049]

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nardenability constituent. Such a moisture curing nature constituent is useful as a sealing agent, a property, especially waterproofing adhesive property further early compared with the conventional [0051]The moisture curing nature constituent of this invention excels [ cure rate ] in an adhesive excellent in waterproofing adhesive property compared with the hardenability constituent of the use the conventional tin system curing catalyst so that clearly from Table 2. The hardenability 8 using the specific tin system curing catalyst of this invention is excellent in the hardening

comparative examples 1, 2, and 3.

Effect of the Invention]It turns out that the hardenability constituent of Examples 1, 2, 3, 4, 5, 6, 7, and performance compared with the hardenability constituent of the comparative examples 1, 2, and 3 which constituent of Examples 1, 2, 3, 4, 5, 6, 7, and 8 is not only excellent in the usual adhesive property but

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JP,2001-139820,A [DETAILED DESCRIPTION] coating agent, and elastic adhesives.

[Translation done.]

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